

# Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/043835

International filing date: 30 December 2004 (30.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US  
Number: 60/538,640  
Filing date: 23 January 2004 (23.01.2004)

Date of receipt at the International Bureau: 09 February 2005 (09.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

1277252

# THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

*January 24, 2005*

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE.**

**APPLICATION NUMBER: 60/538,640**

**FILING DATE: *January 23, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US04/43835***



Certified by

Under Secretary of Commerce  
for Intellectual Property  
and Director of the United States  
Patent and Trademark Office



012304

16085

U.S. PTO

Please type a plus sign (+) inside this box 

Approved for use through 04/30/2003. OMB 0651-0032  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE  
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PTO/SB/16 (5-03)

## PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

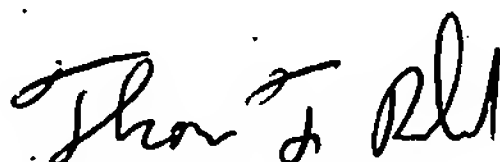
22264 U.S. PTO  
60/538640

012304

INVENTOR(S)					
Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)			
David Alan Jeffrey Lee Ryan Christopher Thomas Dudley	RUSO STRICKER SMITH CULP	AUDUBON, PENNSYLVANIA WYNNEWOOD, PENNSYLVANIA COLLEGEVILLE, PENNSYLVANIA DREXEL HILL, PENNSYLVANIA			
<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (280 characters max) TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number <input type="text"/>		<div>Place Customer Number Bar Code Label here</div>			
OR Type Customer Number here					
<input checked="" type="checkbox"/> Firm or Individual Name		Thomas F. Roland, Esq.			
Address		ATOFINA Chemicals, Inc.			
Address		2000 Market Street, 26th Floor			
City		Philadelphia	State	PA	ZIP 19103
Country		USA	Telephone	215-419-7314	Fax 215-419-7075
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages		16		<input type="checkbox"/> CD(s), Number <input type="text"/>	
<input type="checkbox"/> Drawing(s) Number of Sheets		<input type="text"/>		<input checked="" type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		Claims-3 pages, Abstract-1 page			
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)					
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees				FILING FEE AMOUNT (\$)	
<input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number				01-2717	
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.				\$160.00	
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: _____					

Respectfully submitted,

SIGNATURE



TYPED or PRINTED NAME

Thomas F. Roland, Esq.

TELEPHONE

215-419-7314

Date

01-23-04

REGISTRATION NO.

42,110

(if appropriate)

Docket Number:

IR 3723 PSP

### USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Provisional Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

P19LARGE/REV05



**CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)**

Applicant(s): RUSSO, D. et al

Docket No.

IR 3723 PSP

Serial No.

Not yet assigned

Filing Date

herewith

Examiner

Not yet assigned

Group Art Unit

Not yet assigned

Invention:

**TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME**

I hereby certify that the following correspondence:

Provisional Application for Patent Cover Sheet (in dup.); Certificate of Express mailing; and Provisional Application.

*(Identify type of correspondence)*

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on

January 23, 2004*(Date)*Carol F. Hill*(Typed or Printed Name of Person Mailing Correspondence)**(Signature of Person Mailing Correspondence)*EV 269963534 US*("Express Mail" Mailing Label Number)***Note: Each paper must have its own certificate of mailing.**

**PROVISIONAL APPLICATION COVER SHEET**  
*Additional Page*

PTO/SB/16 (8-00)

Approved for use through 10/31/2002. OMB 0651-0032  
Trademark Office: U.S. DEPARTMENT OF COMMERCE

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

		Docket Number	IR 3723 PSP	Type a plus sign (+) inside this box →	+
INVENTOR(S)/APPLICANT(S)					
Given Name (first and middle [if any])		Family or Surname	Residence (City and either State or Foreign Country)		
Roman Yurevich Gary Stephen		KOROTKOV SILVERMAN	KING OF PRUSSIA, PENNSYLVANIA CHADDS FORD, PENNSYLVANIA		

Number 2 of 2

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

5 APPLICATION FOR  
UNITED STATES LETTERS PATENT

10 of

15 David Alan RUSSO  
Jeffrey Lee STRICKER  
Ryan Christopher SMITH  
Thomas Dudley CULP  
Roman Yurevich KOROTKOV  
and  
20 Gary Stephen SILVERMAN

for

25 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON  
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

30  
35  
40  
45 Attorney Docket No.: IR 3723 PSP

5

10 TRANSPARENT CONDUCTIVE OXIDE FILMS HAVING ENHANCED ELECTRON  
CONCENTRATION/MOBILITY, AND METHOD OF MAKING SAME

15 BACKGROUND OF THE INVENTION

Field of the Invention

20 This invention relates to transparent conductive oxide (TCO) films or coatings, and in particular to new multi- cation, thin film, n-type TCO films in which optimal electron concentration and mobility is achieved by selecting dopants having ionic sizes that approximate those of the oxide host material, and therefore are essentially non-disruptive to the host crystal lattice, thereby reducing electron scattering and increasing film conductivity.

25 The invention also relates to a method of forming TCO films or coatings by atmospheric pressure chemical vapor deposition (APCVD) of soluble solutions with a controlled crystallite size, quality and orientation to yield new n- type TCOs with enhanced electron concentration and mobility, and minimal defects.

30 The improved TCO films of the invention may be used in a variety of applications where performance of the films is affected by electron concentration and/or electron mobility, including solar control films in applications requiring a low plasma wavelength, and ohmic contact films in applications where low-resistivity is critical, such as in wide band gap semiconductor devices.

35

One of the applications of the TCO films or coatings of the invention is for use as solar control coatings, such as might be used on window glass. In general, it is desirable for such coatings to maximize transmittance of visible light while reflecting most infrared and near infrared (NIR) light. The amount of NIR light reflected depends on the  
5 “plasma wavelength,” which in a TCO coating or film is inversely proportional to the electron concentration in the coating. On the other hand, the transmittance of visible light by a TCO coating depends on electron mobility. In order to achieve an effective solar control coating, it is necessary to have a low plasma wavelength (or high plasma frequency), and high electron mobility. However, current thin film coating technologies  
10 permit only one of the two desired properties, electron concentration and electron mobility, to be optimized in a given film.

Much of the present research on thin film TCOs has focused on increasing conductivities, particularly with respect to Indium and/or Cadmium cation combinations. See, e.g., A.J.  
15 Freeman et al., MRS Bulletin, August 2000, pp. 45-51. However, even though In-Cd-O phases have some of the highest room temperature electrical conductivities measured for thin films (3500 S/cm), with mobilities as high as 200 cm<sup>2</sup>/Vs, electron concentrations were only 1x10<sup>20</sup> e/cm<sup>3</sup>, well below the typical 10<sup>21</sup> for doped In<sub>2</sub>O<sub>3</sub> films. On the other hand, some highly conductive In-Ga-Sn-O phases have conductivities as high as 3280  
20 S/cm with measured electron concentrations of 8.6 x 10<sup>20</sup> e/cm<sup>3</sup>, but mobilities of only 24 cm<sup>2</sup>/Vs. Thus, in these prior art materials, either the electron concentration is too low to achieve an optimal plasma wavelength, or the electron mobility is too low to achieve optimal transmittance.

25 Most of the prior films were prepared using low pressure and plasma assisted chemical vapor deposition (CVD), and/or dc or rf sputtering techniques, as opposed to APCVD, as discussed above. Examples of currently used TCOs deposited by sputtering on glass include ZnO:Al, Cd<sub>2</sub>SnO<sub>4</sub>, Zn<sub>2</sub>SnO<sub>4</sub>, ZnSnO<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, WO<sub>3</sub>, and RuO<sub>2</sub>. Examples of currently used TCOs may be deposited by conventional low pressure CVD include  
30 ZnO:In(Al, F, Ga), SnO<sub>2</sub>:F, TiN, and In<sub>2</sub>O<sub>3</sub>:Sn (ITO). The best commercial thin film



TCO coating material,  $\text{In}_2\text{O}_3\text{:Sn}$ , has a plasma wavelength of 1 mm with an electron concentration of  $10^{21} \text{ cm}^{-3}$ .

One of the few approaches to increasing the conductivity of TCO films by using APCVD, as opposed to conventional low pressure CVD or sputtering, is described in U.S. Patent No. 6,524,647 (Varanasi et al.), which discloses APCVD of niobium doped tin oxide films. According to the Varanasi et al. patent, niobium is especially suited for replacing tin in the tin oxide lattice because it has a similar outer shell electron configuration and a comparable atomic number to that of tin. However, Varanasi et al. fails to optimize electrical properties because it fails to recognize that a key factor is actually the ionic size of the dopant, rather than atomic number or outer shell electron configuration.

In contrast, the present invention seeks to enable the ideal balance between electron concentrations, by selection of dopants according to the ionic size of the dopant relative to the oxide matrix, and appropriate control of the APCVD process used to deposit the doped oxides. None of the above-mentioned processes takes into account ionic size for the purpose of optimizing electron concentration and/or electron mobility.

## SUMMARY OF THE INVENTION

It is accordingly a first objective of the invention to overcome the disadvantages of the prior art by providing TCO films having improved electrical properties, and that can be produced in an efficient and cost-effective manner.

25

It is a second objective of the invention to provide TCOs having high visible transmission and improved NIR reflective properties.

It is a third objective of the invention to provide transparent conductive oxides having high conductivity and an optimal combination of electron concentration and electron mobility for a given application.

30

It is a fourth objective of the invention to provide a method of making transparent conductive oxides that permits optimization of electron concentration and electron mobility, in order to improve visible transmission and NIR reflective properties, and/or to provide films having low resistivity and high work function.

It is a fifth objective of the invention to provide a method of using APCVD to deposit TCO films or coatings having improved electrical or optical properties.

These objectives of the invention are accomplished, in accordance with the principles of a preferred embodiment of the invention, by a variety of new n-type TCO films in which the dopants have ionic sizes that approximate those of the metal oxide host material, and that therefore are essentially non-disruptive to the host crystal lattice, reducing electron scattering and increasing film conductivity.

These objectives are further achieved by using atmospheric pressure chemical vapor deposition to deposit soluble solutions having ionic sizes that approximate those of the metal oxide host material to be deposited. The resulting doped metal oxide films have higher conductivities, which in turn imparts better NIR reflective properties to the films than, for example, the current state of the art tin doped indium oxide.

According to a first preferred embodiment of the invention, a metal oxide host, is deposited on a substrate in conventional fashion, but the dopants are chosen to approximately match the ionic size of the host crystals. Suitable hosts, with ionic size given in parentheses, include  $\text{Zn}^{2+}(0.74\text{\AA})\text{O}$ ,  $\text{Sn}^{4+}(0.71\text{\AA})\text{O}_2$ ,  $\text{Ge}^{4+}(0.53\text{\AA})\text{O}_2$ ,  $\text{Zr}^{4+}(0.80\text{\AA})\text{O}_2$ ,  $\text{Ti}^{4+}(0.68\text{\AA})\text{O}_2$ , or  $\text{Ga}^{3+}(0.62\text{\AA})_2\text{O}_3$ , while suitable dopants according to the invention include ions such as  $\text{Sn}^{4+}(0.71)$ ,  $\text{Bi}^{5+}(0.74\text{\AA})$ ,  $\text{Ta}^{5+}(0.73\text{\AA})$ ,  $\text{Hf}^{4+}(0.80\text{\AA})$ ,  $\text{Mo}^{6+}(0.62\text{\AA})$ ,  $\text{Te}^{6+}(0.59\text{\AA})$ ,  $\text{Nb}^{5+}(0.70\text{\AA})$  and the like, all of which have sizes that approximate those of the metal oxide host material. The enhanced conductivity is manifest by both an increase of electron concentration and mobility as measured by the Hall effect.

According to a second preferred embodiment of the invention, a rutile  $\text{MO}_2$  layer is deposited on  $\text{SnO}_2$  or other metal oxide capable of stabilizing the rutile  $\text{MO}_2$  film and optimize near infrared (NIR) reflection in glass/ $\text{SnO}_2$ / $\text{MO}_2$  bilayers and  
5 glass/ $\text{SnO}_2$ / $\text{MO}_2$ / $\text{SnO}_2$  sandwich structures. Suitable rutile  $\text{MO}_2$  materials include but are not limited to  $M = \text{Ti}, \text{V}, \text{Cr}, \text{Mo}, \text{Ru}$ , or mixed alloys thereof.

According to a third preferred embodiment of the invention,  $\text{Sn}_x\text{M}_{1-x}\text{O}_2$  films are deposited on a substrate, where the metal- semiconductor transition of  $\text{MO}_2$  films is  
10 modified by alloying with  $\text{SnO}_2$ , thus optimizing the NIR reflection.

According to a fourth preferred embodiment of the invention, films such as but not limited to  $\text{WO}_3$ ,  $\text{Mo}_x\text{O}_y$ ,  $\text{A}_x\text{WO}_3$ , and  $\text{A}_x\text{Mo}_{1-x}\text{O}_y$  are deposited on a substrate where A is H, Li, Na, and K, and  $x = 0-2$  and high enough to modify the plasma wavelength to  
15 optimize the NIR reflectance. The film properties may be enhanced by APCVD deposition of  $\text{WO}_3$  or  $\text{Mo}_x\text{O}_y$  on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into  $\text{WO}_3$ .

20 Electron concentrations ranging from  $7-10 \times 10^{20} \text{e}/\text{cm}^3$  are possible with the novel n-type TCO films deposited by the above-described processes, as well as electron mobilities of 50-150  $\text{cm}^2/\text{vsec}$ . In addition, these doped metal oxide films can be undercoated with one or more functional layers that can act as barrier layers to ion migration from the glass, anti-iridescent layers to reduce reflected color, and/or nucleation layers to alter the  
25 orientation of the TCO layer(s).

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a table illustrating the properties of  $\text{MO}_2$  compounds with rutile structure  
30 manufactured according to the principles of the first preferred embodiment of the invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be apparent from the examples set forth below, this invention provides a variety  
5 of new n-type TCO films, each having an ideal balance between electron concentration  
and mobility, by selecting dopants that are essentially non-disruptive to the host crystal  
lattice, thereby reducing electron scattering and increasing film conductivity. According  
to the method of the invention, the films are deposited on heated substrates such as glass  
by APCVD of organometallic precursors combined with specific dopants and other  
10 additives such that the deposited films have a higher electron concentration. The higher  
electron concentration is due to the incorporation of dopant ions in the host oxide lattice  
that cause little or no disruption of the lattice parameters, thereby decreasing electron  
scattering and increasing conductivity.

15 In a first preferred embodiment of the invention, doped metal oxide films are prepared by  
APCVD on a suitable substrate, such as soda lime glass, the metal oxides having crystal  
lattice host sizes ranging from .60Å to .80Å. Therefore, according to the principles of the  
invention, the ionic sizes of the dopants are also chosen to be approximately within this  
range. For example, suitable metal oxide hosts include, but are not limited to,  
20  $\text{Zn}^{2+}(\text{0.74}\text{\AA})\text{O}$ ,  $\text{Sn}^{4+}(\text{0.71}\text{\AA})\text{O}_2$ ,  $\text{Ge}^{4+}(\text{0.53}\text{\AA})\text{O}_2$ ,  $\text{Zr}^{4+}(\text{0.80}\text{\AA})\text{O}_2$ ,  $\text{Ti}^{4+}(\text{0.68}\text{\AA})\text{O}_2$ , and  
 $\text{Ga}^{3+}(\text{0.62}\text{\AA})_2\text{O}_3$ , the ionic sizes of which are set forth in the parentheses. Ideal dopants  
for these metal oxide hosts include ions such as  $\text{Sn}^{4+}(\text{0.71})$ ,  $\text{Bi}^{5+}(\text{0.74}\text{\AA})$ ,  $\text{Ta}^{5+}(\text{0.73}\text{\AA})$ ,  
 $\text{Hf}^{4+}(\text{0.80}\text{\AA})$ ,  $\text{Mo}^{6+}(\text{0.62}\text{\AA})$ ,  $\text{Te}^{6+}(\text{0.56}\text{\AA})$ ,  $\text{Nb}^{5+}(\text{0.70}\text{\AA})$  and the like, as well as  
combinations of any of the above-dopants.

25 In a second preferred embodiment of the invention, the principles of the invention are  
applied to hetero-epitaxial growth of APCVD-deposited doped and undoped rutile  $\text{MO}_2$   
structures, where  $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mo}, \text{Ru}$  or mixed alloys thereof, on a  $\text{SnO}_2$  or other  
metal oxide layer suitable for stabilizing the rutile  $\text{MO}_2$  film and optimizing the near  
30 infrared reflection (NIR) in glass/ $\text{SnO}_2/\text{MO}_2$  bilayers and glass/ $\text{SnO}_2/\text{MO}_2/\text{SnO}_2$   
sandwich structures. Some of the  $\text{MO}_2$  materials, such as  $\text{CrO}_2$ ,  $\text{MoO}_2$ ,  $\text{RuO}_2$ , have

metallic conduction with high visible absorption. Others, such as  $\text{TiO}_2$ , are semiconductors with band gaps of 3.0 eV and high visible transparency. Still others, such as  $\text{VO}_2$ , have metal to semiconductor transitions at 340K. In all cases, however, the invention permits modification of the NIR reflectance of the coatings by depositing  
5 glass/ $\text{SnO}_2$ / $\text{MO}_2$  bilayers and glass/ $\text{SnO}_2$ / $\text{MO}_2$ / $\text{SnO}_2$  sandwich structures, where other metal oxides capable of stabilizing the rutile  $\text{MO}_2$  layer may be substituted for  $\text{SnO}_2$ . Since the host materials crystallize in a rutile structure, as illustrated in Fig. 1, it is expected that the deposited  $\text{MO}_2$  films will crystallize in a similar fashion to produce epitaxial like layers. Also, since lattice parameters are close to that of  $\text{SnO}_2$  for most of  
10 these materials, only small stresses are expected in (001) planes.

The third preferred embodiment of the invention involves a variation of the second preferred embodiment in which APCVD is used to grow  $\text{Sn}_x\text{M}_{1-x}\text{O}_2$  ternary alloy system layers that modify the band gap parameters of  $\text{SnO}_2$ . By tuning the fraction of the  
15 transition metal, one can obtain the necessary high NIR reflection with high electron concentration.

Finally, in accordance with the principles of a fourth preferred embodiment of the invention, APCVD is used to grow oxide coatings having the form  $\text{WO}_3$  (as well as  
20 oxides such as  $\text{Mo}_x\text{O}_y$ ) and  $\text{A}_x\text{WO}_3$ , ( $\text{A}_x\text{Mo}_{1-x}\text{O}_y$ ), where A is H, Li, Na, and K, and  $x = 0-2$  and high enough to modify the plasma wavelength to optimize the NIR reflectance. In one embodiment, enhanced film properties are achieved by APCVD deposition of  $\text{WO}_3$  or  $\text{Mo}_x\text{O}_y$  films on soda lime glass substrates with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase incorporation/implantation of A into  
25  $\text{WO}_3$ .

Theoretical studies of  $\text{A}_x\text{WO}_3$  indicate the possibility of a reflectance band shift towards the visible by increasing the fraction  $x$  of alkali metals in the ternary compound. According to a preferred embodiment of the invention, the plasma wavelength of these  
30 coatings is tuned to 0.7  $\mu\text{m}$  by varying the content of alkali metals in the coatings on glass and other substrates. Note that the amount of A is significantly higher than that



used in Li-doped  $\text{WO}_3$  films prepared for their electrochromic properties, where alkali doping is typically less than a few percent. In addition, one can use Na (Li, K) diffusion from glass substrates in APCVD grown  $\text{MO}_y$  films to help promote formation of  $\text{A}_x\text{MO}_3$ . In addition, implantation or vapor deposition of films with A may be used in this embodiment.

A predictive example of the first preferred embodiment of the invention, in which the doped metal oxide is tantalum doped zinc oxide, follows:

#### 10 Predictive Example

A 2.2 mm thick glass substrate (soda lime silica), two inches square, is heated on a hot block to about  $650^\circ\text{C}$ . The substrate may be positioned about 25 mm under the center section of a vertical concentric tube coating nozzle. A carrier gas of dry oxygen flowing at a rate of 12.5 liters per minute (lpm) is then heated to about  $1600^\circ\text{C}$  and passed through a hot wall vertical vaporizer.

A liquid coating solution containing monobutyltin trichloride (MBTC) is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition. A second liquid coating solution of tetraethyl orthosilicate (TEOS) and triethyl phosphite (TEP) in a 1:1 mol ratio is fed to the vaporizer via a syringe pump at a volume flow designed to give a 0.5 mol % concentration in the gas composition.

25 The gas mixture is then allowed to impinge on the glass substrate for about 4 seconds to deposit a mixed oxide of tin and silicon about 80 nm thick with a refractive index of about 1.70. Immediately following, a second gas mixture composed of a diethylzinc tetraethylethylenediamine complex (DEED), a nitrogen carrier gas, tantalum (V) ethoxide, water vapor and air is caused to impinge on the metal oxide coated surface for about 30 seconds, resulting in a tantalum doped zinc oxide film of about 300 nm. The second gas mixture may be formed by mixing separate gas streams in a manifold just

before the coating nozzle. The water vapor and air are introduced at the top of the nozzle to minimize premature reaction with the zinc and tantalum precursors. The DEED liquid is fed via a syringe pump to a second vaporizer through which a nitrogen carrier gas is flowing at 160°C at about 10 lpm. The volume flow is preferably designed to give a 0.5 mol % concentration in the carrier gas.

Finally, the tantalum precursor is fed via a syringe pump to a third vaporizer through which a nitrogen carrier gas is flowing at 180 °C at about 10 lpm. The volume flow is designed to give a 0.1 mol % concentration in the carrier gas. Water is fed via syringe pump into a vaporizer through which an air carrier gas was flowing at about 10 lpm. The vapor concentration is about 3 mols per mol of zinc precursor.

The bilayer film stack made by the above method is predicted to have essentially no reflected color, a visible transmission greater than 70 %, an electron concentration in the range of  $7-10 \times 10^{20} \text{ e/cm}^3$  and a mobility above  $50 \text{ cm}^2/\text{v-sec}$  as measured by the Hall effect.

In a similar manner, hafnium doped zirconium dioxide, molybdenum doped gallium oxide and bismuth/tantalum doped tin oxide films could be prepared. In some cases, the precursors would be placed in heated bubblers and the carrier gas would pass through a molten liquid. These examples are only illustrative of the current invention and one skilled in the art will realize that minor variations outside these embodiments do not depart from the spirit and scope of this invention.

Having thus described various preferred embodiments of the invention in sufficient detail to enable those skilled in the art to make and use the invention, it will nevertheless be appreciated that numerous variations and modifications of the illustrated embodiment may be made without departing from the spirit of the invention. For example, other dopant and host combinations not mentioned herein could be used. Binary and tertiary dopant combinations could be found which might yield films with even higher conductivities. Other undercoat films could be used which have better barrier, anti-

reflection or nucleating layer properties than the combinations described herein. Anti-reflection layers could be placed on top of the doped metal oxide layer. Dopants could be incorporated into the host oxide layer in a gradient fashion; one dopant gradually decreasing while the other gradually increases in a continuum or step fashion. Separate  
5 dopant layers could be combined. The dopants described herein all are intended to replace some of the metal host ions. The enhanced effect might also be accomplished by combining dopants of this invention with dopants such as fluorine that substitute for some of the oxygen atoms in the host matrix.

10 As a result, it is intended that the invention not be limited by the above description, but that it be defined solely in accordance with the appended claims.

What is claimed is:

1. A transparent conductive oxide (TCO) film comprising a doped metal oxide,  
5 wherein the ionic size of at least one dopant in the doped metal oxide  
approximates the size of the host ions in an oxide lattice in the doped metal oxide.
2. The TCO film as claimed in claim 1, wherein the ionic size of said dopant is  
between approximately 0.6Å and 0.8Å.
- 10 3. The TCO film as claimed in claim 2, wherein said metal oxide is selected from  
the group consisting of  $\text{Zn}^{2+}\text{O}$ ,  $\text{Sn}^{4+}\text{O}_2$ ,  $\text{Ge}^{4+}\text{O}_2$ ,  $\text{Zr}^{4+}\text{O}_2$ ,  $\text{Ti}^{4+}\text{O}_2$ ,  $\text{Ga}^{3+}_2\text{O}_3$ , and  
mixtures thereof, and wherein said at least one dopant is selected from the group  
consisting of  $\text{Sn}^{4+}$ ,  $\text{Bi}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{Hf}^{4+}$ ,  $\text{Mo}^{6+}$ ,  $\text{Te}^{6+}$ ,  $\text{Nb}^{5+}$ , and mixtures thereof.
- 15 4. A coated substrate comprising a substrate having directly coated thereon the TCO  
of claim 1.
5. A transparent conductive oxide (TCO) film comprising a rutile metal oxide  $\text{MO}_2$ ,  
20 wherein M is selected from the group consisting of Ti, V, Cr, Mo, Ru, and  
mixtures thereof.
6. The TCO film as claimed in claim 5, further comprising at least one  $\text{M}^1\text{O}_2$  film  
layer, wherein said  $\text{M}^1\text{O}_2$  film layer comprises  $\text{SnO}_2$  or other metal oxide capable  
25 of stabilizing the rutile  $\text{MO}_2$  film.
7. The TCO film as claimed in claim 6, comprising a sandwich structure of  
 $\text{M}^1\text{O}_2/\text{MO}_2/\text{M}^1\text{O}_2$ .
- 30 8. The TCO film as claimed in claim 5, wherein said metal oxide is  $\text{Sn}_x\text{M}_{1-x}\text{O}_2$ ,  
where M is selected from the group consisting of Ti, V, Cr, Mo, and Ru.

9. A coated substrate comprising a substrate having directly coated thereon the TCO of claim 5.
- 5 10. A transparent conductive oxide (TCO) film comprising a metal oxide  $A_xMO_y$  wherein A is selected from the group consisting of H, Li, Na, and K,  $x = 0-2$ , and M is either W or Mo.
- 10 11. A coated substrate comprising a soda lime glass substrate and the TCO film as claimed in claim 10, wherein the metal oxide is deposited on the soda lime glass substrate with consecutive annealing/diffusion of Na, Li and K from the glass, and/or vapor phase with incorporation/implantation of A into  $A_xMO_y$ .
- 15 12. A method of depositing a metal oxide film by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor including at least one dopant having an ionic size that approximates a size of host ions in an oxide lattice in the metal oxide.
- 20 13. The method as claimed in claim 12, wherein the ionic size of said dopant is between approximately  $0.60\text{\AA}$  and  $0.80\text{\AA}$ .
- 25 14. The method as claimed in claim 12, wherein said metal oxide is selected from the group consisting of  $Zn^{2+}O$ ,  $Sn^{4+}O_2$ ,  $Ge^{4+}O_2$ ,  $Zr^{4+}O_2$ ,  $Ti^{4+}O_2$ ,  $Ga^{3+}_2O_3$ , and mixtures thereof, and wherein said at least one dopant is selected from the group consisting of  $Sn^{4+}$ ,  $Bi^{5+}$ ,  $Ta^{5+}$ ,  $Hf^{4+}$ ,  $Mo^{6+}$ ,  $Te^{6+}$ ,  $Nb^{5+}$  and mixtures thereof.
- 30 15. A method of depositing a metal oxide film by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor containing chemical precursors to deposit at least one metal oxide wherein said metal oxide is rutile  $MO_2$ , and M is selected from the group consisting of Ti, V, Cr, Mo, Ru and mixtures thereof.



16. The method of claim 15 wherein multiple metal oxide films are deposited by APCVD, wherein said multiple films comprise  $M^1O_2/MO_2$  bilayers or  $M^1O_2/MO_2/M^1O_2$  sandwich structures, wherein said  $M^1O_2$  film layer comprises  
5  $SnO_2$  or other metal oxide capable of stabilizing the rutile  $MO_2$  film.
17. The method of claim 15 wherein said metal oxide is  $Sn_xM_{1-x}O_2$ , where M is selected from the group consisting of Ti, V, Cr, Mo, and Ru.
- 10 18. A method of depositing metal oxide films by atmospheric pressure chemical vapor deposition (APCVD) on a substrate, comprising the step of exposing the heated substrate to a vapor containing chemical precursors to deposit at least one metal oxide, wherein said metal oxide is  $A_xMO_y$  wherein A is selected from the group consisting of H, Li, Na, and K,  $x = 0-2$ , and M is either W or Mo.

15

Fig. 1. MO<sub>2</sub> compound properties with rutile structure

MO <sub>2</sub>	a, Å	c, Å	V~10 <sup>-23</sup> cm <sup>-3</sup>	N <sub>Site</sub> (Sn) ~10 <sup>22</sup> , cm <sup>-3</sup>	N <sub>Site</sub> (O) ~10 <sup>22</sup> , cm <sup>-3</sup>	% dopant (O)*	E <sub>G</sub> , eV	Thermal Expansion	Plasma ~ <sub>p</sub> , ~ <sub>m</sub>
SnO <sub>2</sub>	4.738	3.187	7.115	2.8	5.6	3.57	3.8	0.02	1.3 (7~10 <sup>20</sup> cm <sup>-3</sup> )
TiO <sub>2</sub>	4.585	2.95	6.2	3.22	6.45	3.1	3.0	0.114	
MnO <sub>2</sub>	4.396	2.871	5.548	3.6	7.2	2.7	Metal	0.05	

5

\* - the required incorporation of a singly charged donor F, Cl, Br on O lattice site to obtain  $n = 2 \sim 10^{21}$  , cm<sup>-3</sup> with the plasma wavelength of 0.77 ~m.

## ABSTRACT OF THE DISCLOSURE

A variety of new n-type TCO films including films with dopants having ionic sizes that approximate those of the metal oxide host material, films with stabilized rutile  
5  $\text{MO}_2$ , and films with  $\text{A}_x\text{MO}_y$ . The films are deposited by APCVD.